SERS IN MICROCHANNELS FROM THE INTEGRATION OF A NANOSTRUCTURED SILVER LAYER BY ELECTRODEPOSITION AND STUDY OF THE PHOTHERMAL EFFECT

Brice Torti, Yannick Hallez, Benjamin Erable and Fabien Chauvet
Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, FRANCE

ABSTRACT

A new method is described and used to integrate an immobilized Surface Enhanced Raman Spectroscopy (SERS) substrate in microchannels. This is based on the direct and fast electrodeposition of an adherent Ag layer on a microchannel wall. This layer exhibits a spatially uniform nanostructure allowing the enhancement of the Raman signal by an analytical factor of 2.10^4 for crystal violet molecules. The microsystem thus elaborated is used to examine the photothermal effect, induced by the laser used, on the SERS spectra under liquid flow.

KEYWORDS: SERS, Photothermal Effect, Electrodeposition, Chemical Imaging, Heat Transfer, Adsorption

INTRODUCTION

Microfluidic devices are developed and used for chemical analysis (detection, identification, and quantification) but also for the study of various physicochemical and biological phenomena under well controlled conditions: spatiotemporal control of the chemical composition, temperature, etc. Associated with this microfluidic control, chemical imaging (mapping of the chemical composition) inside microchannels enables new measurement strategies [1]. This requires a direct chemical imaging method (without labeling) with 3 qualities: sensitivity, spatial resolution and a wide range of addressable species. Among the methods already used in microfluidics, Raman spectroscopy has good spatial and spectral resolution but its sensitivity is too low. The latter can be significantly improved using nanostructured metallic substrates (Ag, Au) for which the plasmon resonance induces the enhancement of Raman scattering in the vicinity of their surfaces [2]. Unlike the usual way of synthetizing such SERS substrates, from metallic nanoparticles (requiring multiple steps, from the synthesis to the controlled deposition by favoring hot spots), here, the nanostructures are directly formed inside microchannels by the electrodeposition of Ag. The efficiency of the elaborated system for microfluidic SERS measurements is evaluated with crystal violet as a model molecule. The cooling effect of the liquid flow in the microchannel, on the SERS signal that comes from the laser-heated substrate, is also examined (photothermal effect [2]).

EXPERIMENTAL

The microfluidic device is elaborated from a double-sided adhesive layer (kapton, 75 µm, digitally cut) bonded between two glass plates (Fig. 1a). The electrodes are first deposited by gold sputtering on the bottom glass plate. A very thin gold layer (non-conductive) is also deposited, between these two electrodes, to favor the adhesion of the electrodeposit on the channel wall during its formation (as in [3]). The latter is performed by a constant current electrolysis of a $AgNO_3$ solution inside the microchannel. A nanostructured, adherent and uniform Ag layer is obtained, Fig. 1c. The formation mechanism of this layer is related to the electrochemical growth of very dense branching deposits on thus gold metallized surfaces [3]. The growth proceeds by re-nucleation processes of nanoscale metal crystals, Fig. 1c. A Raman probe (Ocean Optics) is used to illuminate the Ag layer with a spot size of 158 µm (laser 532 nm, 100 mW), and collect the scattered light which is sent to a spectrometer to obtain Raman spectra, Fig. 1b. Measurements are performed in stagnant solution, or at a liquid flow rate Q, and by recording the spectra over time. The heating, induced by the laser, is estimated by a micro-thermocouple located on the lower surface of the bottom glass plate and 1 mm behind the laser spot, downstream of the flow, Fig. 1b.

RESULTS AND DISCUSSION

In Fig. 2, the obtained SERS spectra and the corresponding temporal variations of the temperature are shown for a stagnant solution Q=0 (Fig. 2a) and Q=10^3 µL/min (Fig. 2b). We observe that the variation of the spectra is correlated with the variation of the temperature. For Q=10^3 µL/min, a steady state regime is reached more rapidly and the temperature increase is lower than for Q=0. From numerical simulation of heat transfer, it is estimated that 10% of the laser power is converted into heat and that the steady state temperature at the laser spot reaches 55°C

and 41°C for Q=0 and Q=10^3 µL/min respectively. Such variations of temperature induce the desorption of crystal violet molecules from the Ag surface and thus the observed decrease of the SERS signal. A more detailed analysis of theses variations (with other concentrations and Q values) provides information on the adsorption of the probed molecules (heat of adsorption). The normal Raman spectrum of crystal violet, obtained with the same optical system but in a UV-Vis cuvette (without surface enhancement), is shown in Fig. 2c; this spectrum was constant over time. The peak intensities (~1000) are of the same order of magnitude as for the steady state SERS spectra (~2500), but the concentration and integration time are higher, Fig. 2c. From these data, we estimate an analytical enhancement factor ([4]) of at least 2.10^4. Furthermore, an uniform SERS signal is measured over the Ag layer.

CONCLUSION

The microfluidic device elaborated, wherein a nanostructured Ag layer is integrated by electrodeposition, enables SERS measurements well suited for chemical imaging in microchannels. The application of a sufficiently fast flow allows to limit the heating of the SERS substrate and thus to maintain intense and stable SERS signals.

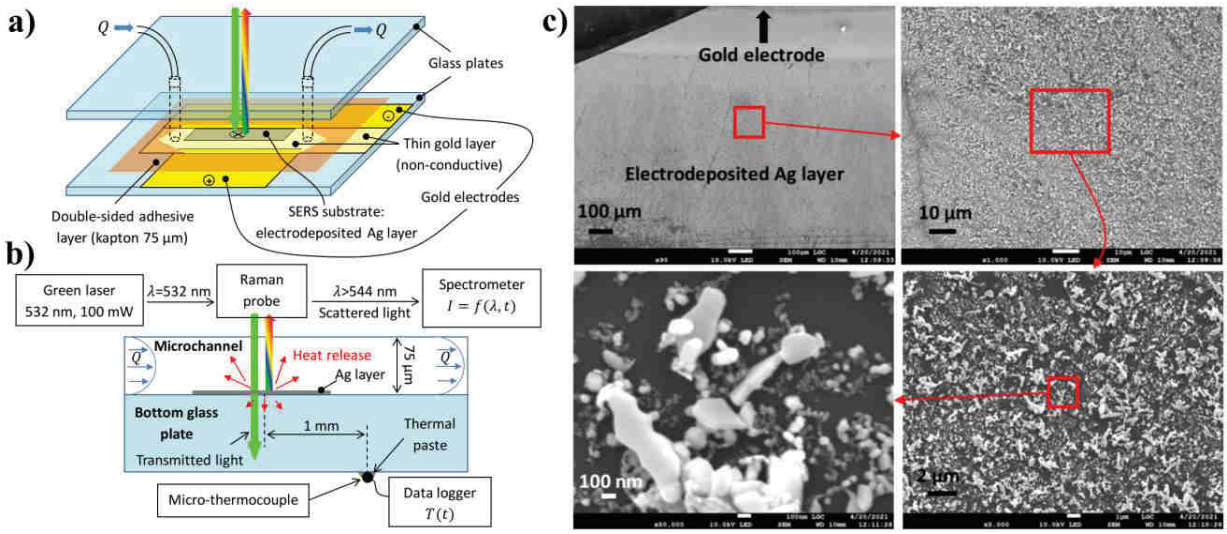

Figure 1: Sketches of the assembly of the microfluidic device (a) and of the running experimental set-up (b) and SEM observations of the electrodeposited silver layer (c).

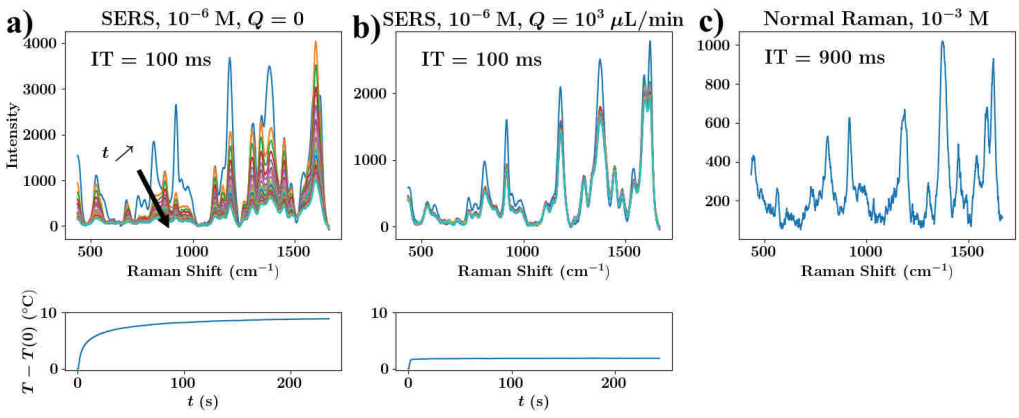

Figure 2: (a,b) Temporal evolutions of SERS spectra of crystal violet and temperature T, after the start of the laser illumination, in stagnant solution (a) and with flow at Q=10^3 µL/min (b); time step between each spectrum is 12 s. (c) Normal Raman spectrum of crystal violet obtained in a UV-Vis cuvette. Baselines have been subtracted. The concentration and integration time (IT) are indicated.

REFERENCES

[1] K.L. A. Chan et al., *Lab on Chip*, 9, 2909-2913, 2009.
[2] K. Kneipp et al., *PRL*, 78, 1667-1670, 1997; Z. Zhang et al., *J. Phys. Chem. C*, 121, 11623-11631, 2017.
[3] V. Fleury et al., *Nature*, 416, 716-719, 2002.
[4] E.C. Le Ru et al., *J. Phys. Chem. C*, 111, 13794-13803, 2007.

CONTACT

F. Chauvet; phone: +33-561 557 468; fabien.chauvet@univ-tlse3.fr